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Efficient and Selective Electron Mediation of Cobalt Complexes with Cyclam and Related Macrocycles in the *p*-Terphenyl-Catalyzed Photoreduction of CO_2

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Abstract: Cobalt(III) complexes of cyclam (cyclam (L_1) = 1,4,8,11-tetraazacyclotetradecane) ($Co^{III}L_1$) or related 14-membered tetraazamacrocycles (L_2–L_8) mediate electron transfer in the photoreduction of CO_2 with *p*-terphenyl (OPP-3) as a photocatalyst and tertiary amines as sacrificial electron donors in methanolic acetonitrile. Tertiary amines (e.g., triethylamine (TEA)) used as electron donors play an important role in the electron mediation of $Co^{III}L_1$ through coordination, and the mediation of the amine-coordinated $Co^{III}L_1$ suppresses the degradative and competitive photo-Birch reduction of OPP-3 and enhances the activity of OPP-3, leading to efficient and selective formation of both carbon monoxide (CO) and formate (HCO_2^-) without producing much H_2. The degradation of OPP-3 is mostly suppressed in the presence of β-hydroxylated tertiary amines such as triethanolamine (TEOA) and tri-2-propanolamine (TIPOA), leading to much more efficient and selective production of CO and HCO_2^-. The total quantum yield of CO and HCO_2^- is 0.25 at 313 nm in the presence of TEOA. Preferential electron transfer from the photoformed radical anion of OPP-3 (OPP-$3^{\bullet-}$) to the TEA-coordinated $Co^{III}L_1$, $[Co^{III}L_1(TEA)_2]^{3+}$, is confirmed by the quenching of OPP-$3^{\bullet-}$ by $[Co^{III}L_1(TEA)_2]^{3+}$ with a diffusion-controlled rate (k_s = 1.1 × 10^{10} M^{-1} s^{-1}). Successive reduction of $[Co^{II}L_1(TEA)]^{2+}$ by OPP-$3^{\bullet-}$ results in the formation of $[Co^IL_1]^+$. $[Co^IL_1]^+$ can react with CO_2 to give $[Co^IL_1(CO_2)]^+$ or react with a proton to give a d^6 hydride $[Co^{III}L_1(H^-)(TEA)]^{2+}$. The extensive charge transfer from metal to bound CO_2 and the coordination of tertiary amines may lead to the formation of d^6 complexes like $[Co^{III}L_1(CO_2^{2-})(TEA)]^+$, which may react with an electron from OPP-$3^{\bullet-}$ or Co(I) species to form CO, OH^-, and Co(II) species such as $[Co^{II}L_1(TEA)]^{2+}$. As for the mechanism for the formation of HCO_2^-, the insertion of CO_2 into intermediary hydride complexes such as $[Co^{III}L_1(H^-)(TEA)]^{2+}$ derived from $[Co^IL_1]^+$ and H^+ is proposed. The structural and electrochemical properties of cobalt complexes of the 14-membered tetraazamacrocycles investigated (L_2–L_8) are also discussed in view of the distribution of the reduction products of CO, HCO_2^-, and H_2.

Introduction

Carbon dioxide fixation is an area of active interest in view of the global greenhouse effect. In particular, photochemical[1] and electrochemical[2] reductions of CO_2 have been extensively studied. A great deal of effort has been devoted to finding effective catalysts for the electroreduction of CO_2, since electroreduction of CO_2 requires potentials more negative than −2.0 V vs SCE. Fisher and Eisenberg[3] reported the electrocatalytic activity of the cobalt(II) and nickel(II) macrocycles for CO_2 reduction yielding CO and H_2 in acetonitrile/water. Sauvage and his collaborators[4] studied a Ni(II)–cyclam (cyclam (L_1) = 1,4,8,11-tetraazacyclotetradecane) complex and found high selectivity toward CO_2 reduction compared to that of H_2O at a mercury electrode. An adsorbed $Ni^IL_1^+$ species was proposed as the active catalyst. This has been independently confirmed by two groups.[5] Porphyrins[6] and phthalocyanines[7] have also been shown to have catalytic activity for the electroreduction of CO_2. The nickel and cobalt macrocycles[8,9] have also been used as catalysts in photoassisted electroreduction of CO_2 at relatively less negative potentials on semiconductor electrodes.

On the other hand, Lehn et al.[10,11] have reported that Ru(2,2′-bipyridine)$_3^{2+}$-catalyzed photoreduction of CO_2 is significantly enhanced in the presence of $CoCl_2$. This enhancement is through the formation of an active catalyst such as $Co(bpy)_n^{2+}$.[12] Tinnemans et al.[13] have also reported the use of cobalt macrocyclic complexes as electron mediators for the photochemical reduction of CO_2 under comparable conditions. Calvin et al.[14] investigated the electron mediation of the $Ni^{II}L_1$ complex for the same photosensitized CO_2 reduction and found quantum yields of 10^{-4}–10^{-3}. The disadvantage of these systems is the competitive H_2 evolution along with the HCO_2^- and CO production.

In order to find whether the CO_2 adducts of the reduced catalysts were intermediates in the CO_2 reduction cycle, several Co(I), Co(II), and Co(III) complexes with macrocyclic ligands and their CO_2 and CO complexes have been investigated spec-

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(1) For instance: (a) Taniguchi, I. *Modern Aspects of Electrochemistry*; Bockris, J. M., White, R. E., Conway, B. E., Eds.; Plenum PublishingCo.: New York, 1989; No. 20, p 327. (b) Willner, I.; Willner, B. *Topics in Current Chemistry*; Springer-Verlag: Berlin and Heidelberg, 1991; Vol. 159, p 153. (c) Henglein, A. *Topics in Current Chemistry*; Springer-Verlag: Berlin and Heidelberg, 1988; Vol. 143, p 113. (d) Bahnemann, D. W. *Photochemical Conversion and Storage of Solar Energy*; Pelizzetti, Schlavello, M., Eds.; Kluwer Academic Publishers: The Netherlands, 1991; p 251. (e) Mandler, D.; Willner, I. *J. Am. Chem. Soc.* **1987**, *109*, 7884. (f) Cook, R. L.; MacDuff, R. C.; Sammells, A. F. *J. Electrochem. Soc.* **1988**, 3069. (g) Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004. (h) Isida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1988**, 339. (i) Willner, I.; Mandler, D. *J. Am. Chem. Soc.* **1989**, *111*, 1330. (j) Ishida, H.; Terada, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1990**, *29*, 905.

(2) (a) Inoue, S. *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodansha Ltd. and Wiley: Tokyo and New York, 1982; p 253. (b) Ulman, M.; Aurian-Blajeni, B.; Halman, M. *CHEMTECH*. **1983**, 235 and references cited therein. (c) Silvesttri, G. *Carbon Dioxide as a Source of Carbon*; Aresta, M., Forti, G., Eds.; NATO ASI Ser., 1987; p 339. (d) Silvestri, G.; Gambino, S.; Filardo, G. *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization*; Aresta, M., Schloss, J. V., Eds.; Kluwer Academic Publishers: The Netherlands, 1990; p 101. (e) Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H.; O'Toole, T. R.; Downard, A.; Meyer, T. J. *Organometallics* **1988**, *7*, 238. (f) Arai, G.; Harashina, T.; Yasumori, I. *Chem. Lett.* **1989**, 1215. (g) Tanaka, K.; Matsui, T.; Tanaka, T. *J. Am. Chem. Soc.* **1989**, *111*, 3765. (h) Sugimura, K.; Kuwabata, S.; Yoneyama, H. *J. Am. Chem. Soc.* **1989**, *111*, 2361. (i) Rasmussen, S. C.; Richter, M. M.; Yi, E.; Place, H.; Brewer, K. J. *Inorg. Chem.* **1990**, *29*, 3926. (j) Bockris, J. O'M.; Wass, J. C. *J. Electrochem. Soc.* **1989**, *136*, 2521. (k) Garnierr, L.; Rollin, Y.; Perichon, J. *New J. Chem.* **1989**, *13*, 53. (l) Hammouche, M.; Lexa, D.; Momenteau, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 8455. (m) Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 86. (n) Komeda, N.; Nagao, H.; Matsui, T.; Adachi, G.; Tanaka, K. *J. Am. Chem. Soc.* **1992**, *114*, 3625. (o) Summers, D. P.; Frese, K. W., Jr. *J. Electrochem. Soc.* **1988**, *135*, 264. (p) Nakagawa, S.; Kudo, A.; Azuma, M.; Sakata, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *308*, 339.

(3) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.

(4) (a) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315. (b) *J. Am. Chem. Soc.* **1986**, *108*, 7461. (c) Collin, J.-P.; Jouaiti, A.; Sauvage, J.-P. *Inorg. Chem.* **1988**, *27*, 1986.

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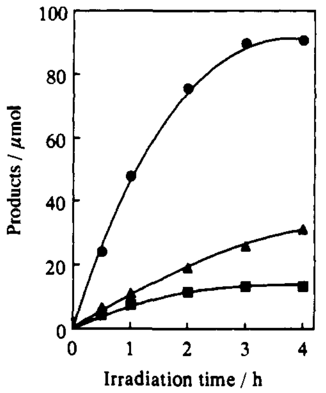
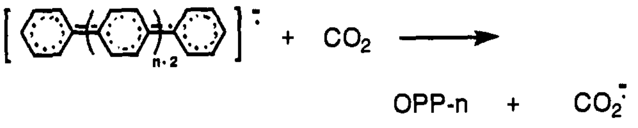


Figure 1. Photochemical reduction of CO_2 in the OPP-3/Co^{III}cyclam/TEA/MeOH/AN system: ●, CO; ▲, HCO_2^-; ■, H_2.

Scheme I



trochemically and electrochemically.[15–20] Some Co(I) complexes with tetraazamacrocycles were found to be active for binding CO_2 and CO, and the thermodynamic and kinetic behaviors of their formation were elucidated by spectrometric and electrochemical methods.[21–23]

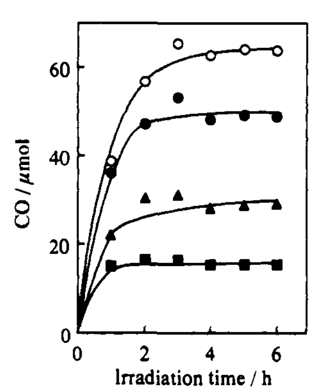


Figure 2. CO evolution as a function of molar concentration of Co^{III}cyclam in the OPP-3/TEA/MeOH/AN system. [Co^{III}cyclam]: 1.7 mM (○); 1.3 mM (●); 0.8 mM (▲); 0.4 mM (■).

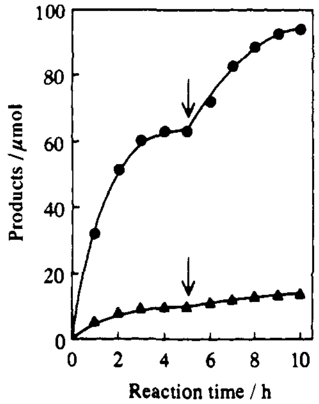


Figure 3. Generation of CO (●) and H_2 (▲) in OPP-3 (10 mg)/Co^{III}L$_I$/TEA/MeOH/AN. A fresh amount of OPP-3 (10 mg) was added after 5 h of irradiation (arrow).

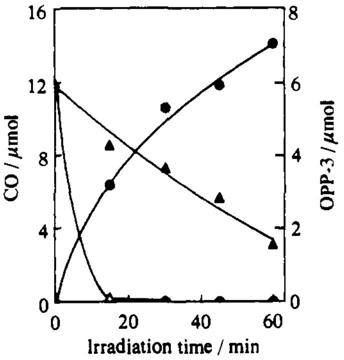


Figure 4. Effect of Co^{III}L$_I$ addition on CO evolution (○, ●) and consumption of OPP-3 (△, ▲) in the TEA/MeOH/AN system: ○, ▲, without Co^{III}L$_I$; ●, ▲, with Co^{III}L$_I$.

Recently, we clarified in our studies on photocatalysis of oligo(*p*-phenylenes) (OPP-*n*) that OPP-*n* compounds ranging from *p*-terphenyl (OPP-3) to *p*-sexiphenyl (OPP-6) catalyze the photoreduction of CO_2 to HCO_2^- with triethylamine (TEA) as a sacrificial electron donor in a dried aprotic polar solvent like *N*,*N*-dimethylformamide (DMF) and acetonitrile (AN).[24] The photoreduction was shown to proceed via direct electron transfer from the photogenerated quinoidlike radical anion of OPP-n$^{\bullet-}$ to the CO_2 molecule as shown in Scheme I.[25]

Because of the reported role in CO_2 activation by metal macrocyclic complexes, we investigated the effectiveness of these complexes as electron mediators or carriers in the OPP-3-catalyzed photoreduction of CO_2. As reported in a preliminary paper,[26] the efficiency in the OPP-3-catalyzed CO_2 photoreduction was enhanced, and CO was found to form selectively when Co^{III}cyclam Co^{III}L$_I$) was employed as an activator of CO_2 with β-hydroxylated tertiary amines as electron donors. In this paper, we present detailed studies on the catalytic electron mediation of cobalt

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(5) (a) Balazs, G. B.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1992**, *322*, 325. (b) Fujihira, M.; Hirata, Y.; Suga, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *292*, 199.

(6) Takahashi, K.; Hiratsuka, K.; Sasaki, H. *Chem. Lett.* **1979**, 305.

(7) (a) Meshitsuka, S.; Ichikawa, M.; Tameru, K. *J. Chem. Soc., Chem. Commun.* **1974**, 158. (b) Hiratsuka, K.; Takahashi, K.; Sasaki, H.; Toshima, S. *Chem. Lett.* **1977**, 1137.

(8) Bradley, M. G.; Tysak, T.; Graves, D. J.; Vlachopoulos, N. A. *J. Chem. Soc., Chem. Commun.* **1983**, 349.

(9) Beley, M.; Collin, J.-P.; Sauvage, J.-P.; Petit, J.-P.; Chartier, P. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *206*, 333.

(10) (a) Lehn, J.-M.; Ziessel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 271.

(11) (a) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. (b) Ziessel, R.; Hawecker, J.; Lehn, J.-M. *Helv. Chim. Acta* **1986**, *69*, 1065.

(12) (a) Krishnan, C. V.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 2141. (b) Krishnan, C. V.; Brunschwig, B. S.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1985**, *107*, 2005. (c) Krishnan, C. V.; Creutz, C.; Mahajan, D.; Schwarz, H. A.; Sutin, N. *Isr. J. Chem.* **1982**, *22*, 98.

(13) Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. H. M. W.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 288.

(14) (a) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105. (b) Craig, C. A.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1990**, *94*, 7957.

(15) Rillema, D. P.; Endicott, J. F.; Papaconstantinou, E. *Inorg. Chem.* **1971**, *10*, 1739.

(16) Roche, T. S.; Endicott, J. F. *Inorg. Chem.* **1974**, *13*, 1575.

(17) Hay, R. W.; Lawrence, G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1466.

(18) (a) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 86. (b) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 4029. (c) Tait, A. M.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 966. (d) Tait, A. M.; Lovecchio, F. V.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 2206.

(19) Kildahl, N. K.; Viriyanon, P. *Inorg. Chem.* **1987**, *26*, 4188.

(20) (a) Szalda, D. J.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1989**, *28*, 1446. (b) Szalda, D. J.; Schwarz, C. L.; Endicott, J. F.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1989**, *28*, 3214.

(21) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870.

(22) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 1153.

(23) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343.

(24) Matsuoka, S.; Kohzuki, T.; Pac, C.; Yanagida, S. *Chem. Lett.* **1990**, 2047.

(25) Matsuoka, S.; Kohzuki, S.; Pac, C.; Ishida, A.; Takamuku, S.; Kusaba, M.; Nakashima, N.; Yanagida, S. *J. Phys. Chem.* **1992**, *96*, 4437.

(26) Matsuoka, S.; Yamamoto, K.; Pac, C.; Yanagida, S. *Chem. Lett.* **1991**, 2099.

Table I. Photochemical Generation of CO, HCO_2^-, and H_2 from OPP-3, $Co^{III}L_1$, TEA, and CO_2 in a MeOH/AN System[a]

			amt of product/μmol			ratio	
run	[OPP-3]/mM	$[Co^{III}L_1]$/mM	CO	HCO_2^-	H_2	CO/HCO_2^-	$(CO + HCO_2^-)/H_2$
1	2.0	1.7	24	12	3.7	2.0	9.7
2	2.0	0	0	0	0		
3	2.0	0.83	14	6.0	2.4	2.2	8.3
4	0.5	1.7	12	11	2.3	1.1	10
5	0	1.7	0	0	0.02		0
6[b]	2.0	1.7	0	0	0		
7[c]	2.0	1.7	0	0	47	0	0
8[d]	2.0	1.7	2.8	7.5	1.5	0.37	6.9
9[c,d]	2.0	1.7	0	0	87	0	0
10	2.0	1.7 ($CoCl_2$)	0	0	2.4	0	0
11	2.0	1.7 (Ni(II)L_1)	0	0	0.17	0	0

[a] A 3-mL $TEA/CH_3OH/CH_3CN$ (1/1/4) solution with CO_2 was irradiated at $\lambda > 290$ nm for 1 h. [b] In the absence of TEA. [c] Under argon atmosphere. [d] In aqueous AN (H_2O, 0.5 mL; AN, 2.0 mL).

complexes of cyclam (L_1) or several related 14-membered tetraazamacrocycles (L_2–L_8) in CO_2 photoreduction using OPP-3.

Results and Discussion

OPP-3-Catalyzed Photoreduction of CO_2 in the Presence of Co^{III}cyclam ($Co^{III}L_1$). Because of the low solubility of $Co^{III}L_1$ in acetonitrile, the OPP-3-catalyzed photoreduction of CO_2 was carried out in a methanolic AN solution with TEA as an electron donor (1/4/1). Figure 1 shows time-conversion plots for the formation of CO, HCO_2^-, and H_2 in the presence of $Co^{III}L_1$ with an excess of OPP-3 (10 mg) under $\lambda > 290$ nm irradiation. Interestingly, CO evolution was found to be efficient and formed with a much greater yield than HCO_2^- and H_2, compared with the photoreduction in the absence of $Co^{III}L_1$ in AN.[25] Mass spectroscopy and ^{13}C NMR confirmed the formation of ^{13}CO (m/z = 29) and $H^{13}CO_2^-$ (δ = 169.3 ppm) in the photoreduction of $^{13}CO_2$.

Figure 2 shows the dependence of CO production on the concentration of $Co^{III}L_1$ in the OPP-3 (10 mg)/TEA/MeOH/AN system. With an increase of $Co^{III}L_1$ concentration, the rate of CO evolution increased, and the formation leveled off after reaching an amount of CO proportional to the quantity of $Co^{III}L_1$; the maximum quantity of CO produced (60 μmol) was more than 10 times the quantity of the $Co^{III}L_1$ used (5.2 μmol). Furthermore, after reintroducing CO_2 into the reaction system at the leveling-off point, the formation of CO was recovered to some extent.

In order to learn why the production of CO levels off, the CO production was monitored continuously over a period of 10 h under similar conditions (OPP-3 (10 mg)/$Co^{III}L_1$/TEA/MeOH/AN system), as shown in Figure 3. After initial efficient CO evolution (32 μmol in 1 h), the rate decreased gradually and leveled off in 5 h. At this point, the reaction was stopped, and 10 mg of OPP-3 was added to the reaction system. On continued irradiation, the CO formation was recovered with slightly decreased rate. These results suggest that the gradual decrease in the CO formation is mainly due to degradation of OPP-3 through the photo-Birch reduction.[25,27]

The photolysis with $Co^{III}L_1$ was investigated in a homogeneous methanolic AN solution of OPP-3 (3×10^{-3} M) in order to elucidate the effect of $Co^{III}L_1$ on the dissolved OPP-3 under protic conditions. It is interesting to note that in the absence of $Co^{III}L_1$, OPP-3 disappears from the methanolic system after 15 min of irradiation. However, the presence of $Co^{III}L_1$ retarded the disappearance of OPP-3 from the system, and the cyclam was present without degradation (Figure 4). These observations suggest that protic species enhance the photo-Birch reduction leading to the consumption of OPP-3 but that the presence of $Co^{III}L_1$ suppresses the degradation of OPP-3 even under protic conditions.

Table I summarizes the results of irradiating homogeneous solutions of OPP-3 and $Co^{III}L_1$ under various conditions. When a CO_2-saturated homogeneous solution of OPP-3 and $Co^{III}L_1$ in TEA/MeOH/AN was irradiated for 1 h at $\lambda > 290$ nm, CO was formed as a main product with smaller quantities of HCO_2^- and H_2 (run 1). In the absence of $Co^{III}L_1$, OPP-3, or TEA in control experiments, neither CO nor HCO_2^- was detected (see runs 2, 5, and 6). When the concentrations of OPP-3 and $Co^{III}L_1$ were decreased by factors of 2 and 4, respectively (runs 3 and 4), the amounts of CO and HCO_2^- decreased, but product selectivity in both cases was comparable with the selectivity obtained under the initial conditions.

As elucidated previously,[25] OPP-3 undergoes gradual photo-Birch reduction during photocatalysis in aprotic DMF solution. The turnover number of the catalytic cycle was determined to be 4 for the formation of HCO_2^- on the basis of the amount of OPP-3 consumed after photoreaction in DMF for 1 h. When $Co^{III}L_1$ was present during photoreduction in methanolic AN, however, the turnover numbers were determined to be 5 (CO), 2 (HCO_2^-), and 1 (H_2). Further, when the concentration of OPP-3 was diluted by a factor of 4 in the presence of the same concentration of $Co^{III}L_1$, the turnover numbers for CO, HCO_2^-, and H_2 were increased to 9, 8, and 2, respectively (run 4). These observations can be explained as arising from the effective suppression of the photo-Birch reduction by $Co^{III}L_1$.

Another important role of $Co^{III}L_1$ is the suppression of H_2 evolution. In other words, the present system enhances the selectivity shown by $(CO + HCO_2^-)/H_2$ ratios to give values from 7 to 10. These ratios are independent of the concentrations of both OPP-3 and $Co^{III}L_1$ (runs 3 and 4). In the absence of CO_2, H_2 evolved very effectively in the system (run 7). When the photolysis was carried out using MeOD instead of MeOH, the hydrogen evolved in the presence and absence of CO_2 was found to be a mixture of D_2, DH, and H_2 in the ratios 33/48/19 and 26/44/30, respectively. These observations suggest that the proton source for H_2 evolution is not only the methanol solvent but also the TEA chosen as the electron donor.

In order to confirm the selectivity under more protic conditions, the photoreaction was carried out in the presence of H_2O (run 8). Although the efficiency decreased to a fair extent and the formation of HCO_2^- increased, the photoreduction of CO_2 occurred in preference to reduction of H_2O to H_2. Further, in the absence of CO_2, the photoreduction of water occurred very efficiently to yield 87 μmol of H_2 in 1 h (run 9).

The catalytic electron mediation in the OPP-3-catalyzed CO_2 photoreaction was extended to some other metallic species. Neither $CoCl_2$ (run 10) nor cyclam complexes of Ni(II) (run 11), Zn(II), Fe(II), and Cu(II) functioned as electron mediators for CO_2 photoreduction. The failure in the case of $Ni^{II}L_1$ is in marked contrast with its excellent performance as an electron mediator in the electroreduction[4] and the photochemical reduction[14] of CO_2.

Effect of Tertiary Amines on Electron Mediation of Co^{III}cyclam ($Co^{III}L_1$). The photoreduction with TEA was extended to other tertiary amines as electron donors, since Lehn et al. reported that tertiary amines influence $Ru(bpy)_3^{2+}$-photosensitized reduction of CO_2 to some extent.[10-12] This was also found to be true for the present system. When β-hydroxylated tertiary amines such as triethanolamine (TEOA) and tri-2-propanolamine (TIPOA) were used instead of TEA as electron donors, the quantity of CO markedly increased, and the formation curves were asymptotic

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(27) Barltrop, J. A. *Pure Appl. Chem.* **1973**, *33*, 179.

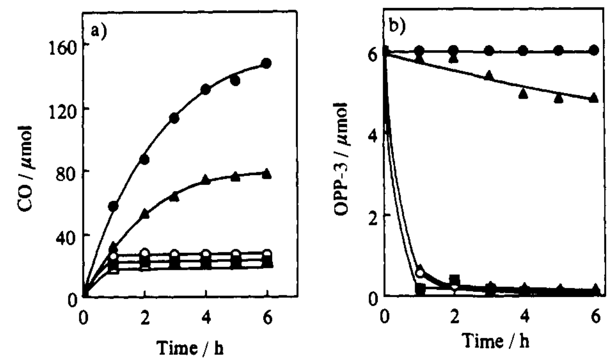

Figure 5. CO evolution (a) and consumption of OPP-3 (b) in photolysis of the OPP-3/$Co^{III}L_1$ system with various tertiary amines: △, TEA; ○; TPA; ■, TBA; ▲, TEOA; ●, TIPOA.

Table II. Effects of Various Tertiary Amines on Photochemical Generation of CO, HCO_2^-, and H_2 from OPP-3, $Co^{III}L_1$, and CO_2 in MeOH/AN[a]

		amt of product/μmol			product ratio	
run	amine	CO	HCO_2	H_2	CO/ HCO_2^-	(CO + HCO_2^-)/ H_2
12	TEA	24	12	3.7	2.0	9.7
13	TPA[b]	26	18	2.6	1.4	17
14	TBA[c]	21	16	2.2	1.3	17
15	TEOA[d]	52	30	3.4	1.7	24
16	TIPOA[e]	63	18	5.0	3.5	16
17	DEAEO[f]	32	25	4.0	1.3	14
18	DEAIPO[g]	43	25	3.3	1.7	21

[a] Homogeneous solutions (3 mL) were irradiated at >290 nm for 1 h. [b] Tri-*n*-propylamine. [c] Tri-*n*-butylamine. [d] Triethanolamine. [e] Tri-2-propanolamine. [f] 2-(Diethylamino)ethanol. [g] 1-(Diethylamino)-2-propanol.

after 4 or 6 h of irradiation as shown in Figure 5a. Interestingly, the degradation of OPP-3 was almost suppressed in the presence of TIPOA as shown in Figure 5b. The leveling-off of the formation of CO was ascribed to the effective consumption of CO_2.

In Table II are summarized the product analyses and product ratios of CO/HCO_2^-, CO/H_2, and $(CO + HCO_2^-)/H_2$ in each 1-h photolysis. When TEA was replaced by longer alkylamines like tri-*n*-propylamine (TPA) and tri-*n*-butylamine (TBA), introduction of CO_2 caused separation of each reaction mixture into two phases. However, the total quantity of CO and HCO_2^- was comparable, and the ratio of $(CO + HCO_2^-)/H_2$ increased with increased alkyl chain length from ethyl to butyl (runs 12–14), suggesting strongly preferential reduction of CO_2. Remarkable increases in the formation of CO and HCO_2^- were observed when some β-hydroxylated amines were chosen as electron donors (runs 15–18). Interestingly, the hydroxylated trialkylamines enhanced the formation not only of CO but also of HCO_2^-. In particular, triethanolamine (TEOA) and tri-2-propanolamine (TIPOA) led to much more efficient photoreduction to CO and HCO_2^- (runs 15 and 16).

Very high quantum yields, 0.15 and 0.10, were obtained for the formation of CO and HCO_2^-, respectively, in the presence of TEOA at 313 nm. The total quantum yield (0.25) for the CO_2 reduction is more than 3 times higher than that of the OPP-3-catalyzed CO_2 photoreduction with TEA in the absence of $Co^{III}L_1$.[25] In addition, the suppression of H_2 evolution and the selectivity in production of CO in the presence of TIPOA are worth noting. With regard to the amines tested, the following orders were obtained under our conditions: TIPOA = TEOA > DEAIPO > DEAEO > TPA > TBA = TEA for the total yield of CO and HCO_2^-; TIPOA > TEA > TEOA > DEAIPO > TPA > DEAEO = TBA for the selectivity of CO formation shown by the ratio CO/HCO_2^-.

Spectral Studies on Electron Mediation of Co^{III}cyclam ($Co^{III}L_1$). It should be noted that $Co^{III}L_1$ has weak absorption due to the d–d transition (λ_{max} = 620 nm, ϵ = 38) along with a strong absorption at λ_{max} = 290 nm. Furthermore, the absorption spectra of $Co^{III}L_1$ in the presence of OPP-3 and TEA were obtained under a CO_2 atmosphere before and after irradiation with a Hg arc lamp for 30 min, as shown in Figure 6a. The d–d transition absorption at λ_{max} = 620 nm shifts to a shorter wavelength (λ_{max} = 580 nm) in the presence of TEA before irradiation, as shown in Figure 6a. This fact suggests ligand exchange of chlorine atoms at the axial position of $[Co^{III}L_1Cl_2]Cl$ with TEA. The $Co^{III}L_1$ complex in the presence of TEA is abbreviated as $[Co^{III}L_1(TEA)_2]^{3+}$ hereafter.

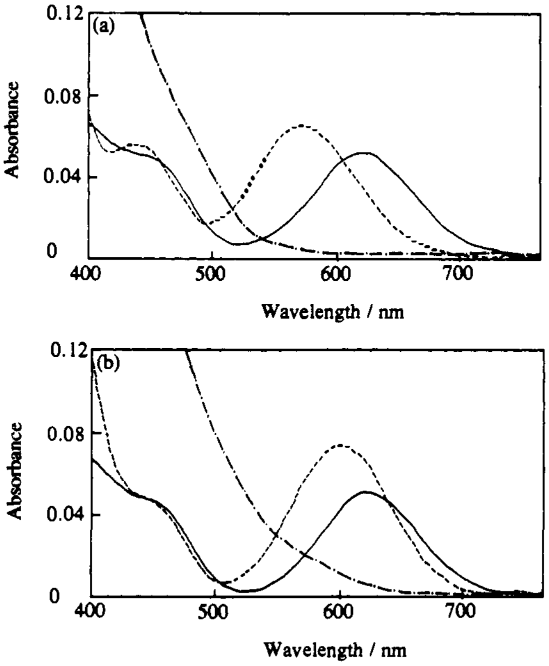

Figure 6. Absorption spectra of $Co^{III}L_1$ in the presence of OPP-3 and amines, TEA (a) or TEOA (b), before and after irradiation under CO_2: —, without amine; - - -, with amine before irradiation; –·–, with amine after irradiation for 10 min.

After irradiation for 30 min, the d–d transition absorption disappeared completely and was followed by the formation of CO and HCO_2^-. The disappearance of the d–d transition absorption was ascribed to the reduction of Co(III) to Co(II). In addition, when TEOA was used instead of TEA, the d–d transition absorption maximum was observed at λ_{max} = 605 nm, whose shift to the shorter wavelength was less than that in the case of TEA, as shown in Figure 6b. This fact suggests that the effect of β-hydroxylamines on the photoreactions should arise from ligating ability rather than difference in electron-donating ability. In fact, oxidation potentials of TEOA and TEA are quite similar.[11b]

In order to know the valence state of key cobalt species in the electron mediation, i.e., Co(II) or Co(I), ESR spectroscopy was investigated at 77 K after photolysis of a methanolic AN solution containing OPP-3, $Co^{III}L_1$, and TEA or TEOA in the presence or absence of CO_2. Figure 7a shows an ESR spectrum of the photolysate in the presence of TEA and CO_2 under $\lambda > 290$ nm light irradiation for 5 min. Obviously, a sharp eight-line spectrum was observed due to the cobalt(II) nuclear spin ($I = {}^7/_2$) as reported.[28] Surprisingly, ESR parameters shown in Figure 7a are quite comparable with those of the five-coordinate Co(II) complex with the monoanion of dimethylglyoxime (Hdmg) and pyridine (py), i.e., $[Co(Hdmg)_2(py)]^{2+}$: $g_{\parallel} = 2.0137$, $A_{\parallel} = 86.5$ G; $g_{\perp} = 2.24$, $A_{\perp} = 15.0$ G.[29] The consistency in ESR parameters strongly supports the photoformation of the stable five-coordinate complex, which can be expressed as $[Co^{II}L_1(TEA)]^{2+}$.

In addition, when TEA was replaced by TEOA, each signal became broadened compared with those in the case of TEA (Figure 7b). These facts strongly suggest the effective photo-

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(28) Kohno, M.; Ohya-Nishiguchi, H.; Yamamoto, K.; Sakurai, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 932.

(29) Rockenbauer, A.; Buds-Zahonyi, E.; Simandi, L. *J. Chem. Soc., Dalton Trans.* **1975**, 1729.

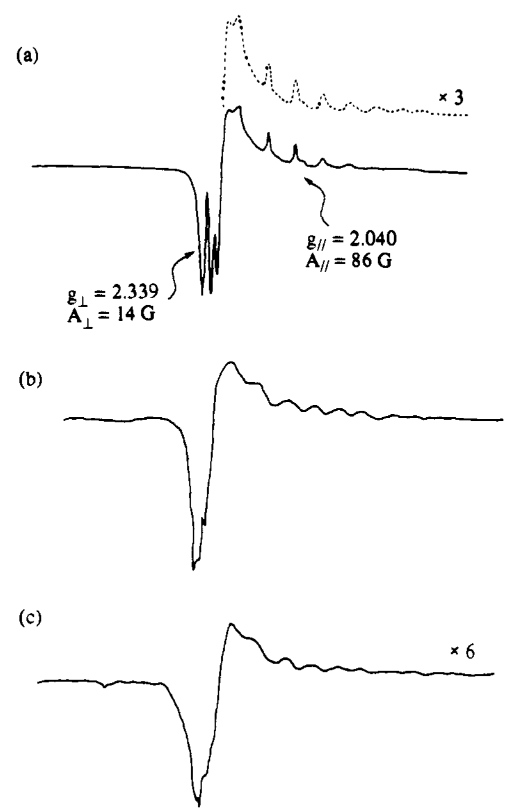

Figure 7. ESR spectra observed at 77 K in the photolysis of OPP-3 and $Co^{III}L_1$ (a) in the presence of TEA and CO_2, (b) in the presence of TEOA and CO_2, and (c) in the presence of TEA for 5 min.

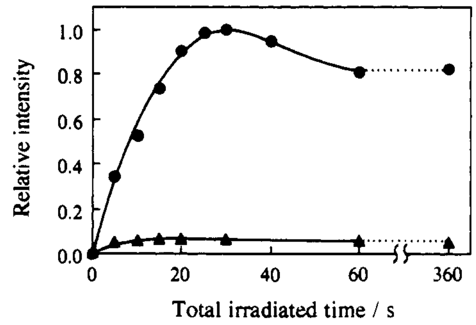

Figure 8. Correlation between the signal intensity and the time of UV irradiation ($\lambda > 290$ nm) of the CO_2/OPP-3/$Co^{III}L_1$/TEA system (●) or the OPP-3/$Co^{III}L_1$/TEA system (▲).

formation of the five-coordinate Co(II) species in the presence of TEOA. On the other hand, weak signals were observed when the OPP-3/$Co^{III}L_1$/TEA system was irradiated in the absence of CO_2 (Figure 7c), whose intensity decreased during repeated measurements.

In order to know how rapidly the five-coordinate Co(II) species are formed in the $Co^{III}L_1$-mediated electron-transfer processes, the relative intensity of the Co(II) signal in ESR was monitored in the presence and absence of CO_2 (Figure 8). To our surprise, the Co(II) species was formed immediately after irradiation in the presence of CO_2, and the intensity increased gradually and leveled off after 30-s irradiation, while the weak signal in the absence of CO_2 was unchanged in the same time scale. These observations make it clear that the five-coordinate Co(II) species such as $[Co^{II}L_1(\text{TEA or TEOA})]^{2+}$ should be formed firmly in the present photoreduction of CO_2.

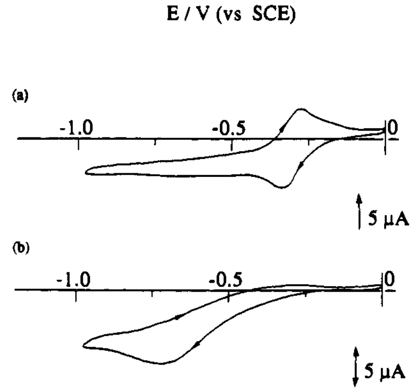

Figure 9. Cyclic voltammograms of $Co^{III}L_1$ ($[Co^{III}L_1Cl_2]Cl$) (2×10^{-4} M) in AN/TBAP-saturated solution (0.1 M) under N_2 (glassy carbon electrode (0.3 cm^2); scan rate 100 mV s^{-1}): (a) in the absence of tertiary amines; (b) in the presence of TEA (0.7 M).

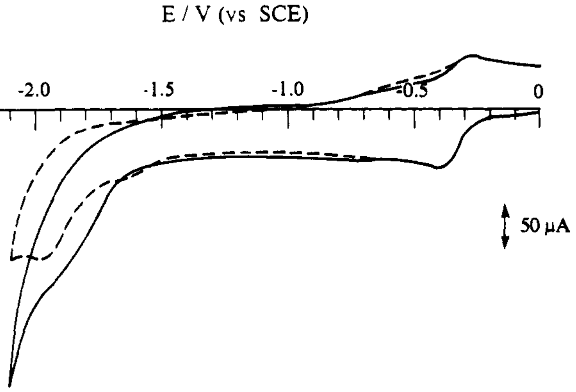

Figure 10. Cyclic voltammograms of $[Co^{III}L_1Cl_2]ClO_4$ in AN/TPAP-saturated solution under Ar or CO_2 (glassy carbon electrode (0.28 cm^2); scan rate 500 mV s^{-1}): —, in the presence of CO_2; ---, in the absence of CO_2.

Electrochemical Studies on Electron Mediation of Co^{III}cyclam ($Co^{III}L_1$). Electrochemical experiments were performed in order to clarify the effect of tertiary amines on the electron mediation. A cyclic voltammogram of $Co^{III}L_1$ in AN under N_2 is shown in Figure 9a. In the absence of tertiary amines, the $Co^{III}L_1/Co^{II}L_1$ couple is reversible as shown, the redox potential being determined to be −0.31 V vs SCE. An irreversible wave was observed for the $Co^{III}L_1/Co^{II}L_1$ couple when TEA (Figure 8b) was added to the CO_2-free $Co^{III}L_1$ system. In addition, the cathodic peak shifts more negatively to become −0.69 V. The case was also true for the presence of TEOA (cathodic peak shift: −0.73 V). The structural change in $Co^{III}L_1$ confirmed by cyclic voltammetry can be explained as due to ligand exchange in the $Co^{III}L_1$ complex in the presence of TEA or TEOA.

Cyclic voltammograms for the $Co^{II}L_1/Co^{I}L_1$ couple were also determined in the absence and presence of CO_2 in AN under Ar (Figure 10). An irreversible peak ascribed to the $Co^{II}L_1/Co^{I}L_1$ couple was observed at −1.9 V. Further, in the presence of CO_2, the cathodic current began around −1.70 V, suggesting that the CO_2 reduction is mediated by $Co^{I}L_1$ species, not by $Co^{II}L_1$ species.

Structural Effects of 14-Membered Tetraazamacrocycles in Their Cobalt Complexes. In order to investigate structural effects of Co(III) or Co(II) macrocycles on their electron mediation, some unsaturated or methylated derivatives of cyclam were synthesized, and their cocatalytic effect on OPP-3-catalyzed CO_2 photoreduction was examined using TEA or TEOA as the electron donor. The abbreviations and structures of the macrocycles examined are shown in Figure 11.

Product distributions in CO_2 photoreduction with various Co(III) or Co(II) complexes as electron mediators and TEA or TEOA as sacrificial electron donors are summarized in Table III. Ratios of $CO/(HCO_2^- + H_2)$ and HCO_2^-/H_2 are also shown along with redox potentials of the Co(II)/Co(I) couples in AN to clarify the structural effects. With respect to $[Co^{III}L_1Cl_2]Cl$ ($Co^{III}L_1$), replacement of Cl atoms with Br atoms or ClO_4 ions did not affect the photoreduction in the presence of TEA or TEOA as the electron donor (runs 19–21).

Some partially unsaturated, 14-membered tetraazamacrocycles with two or four C-methyl groups (L_2, L_3, L_4) also gave com-

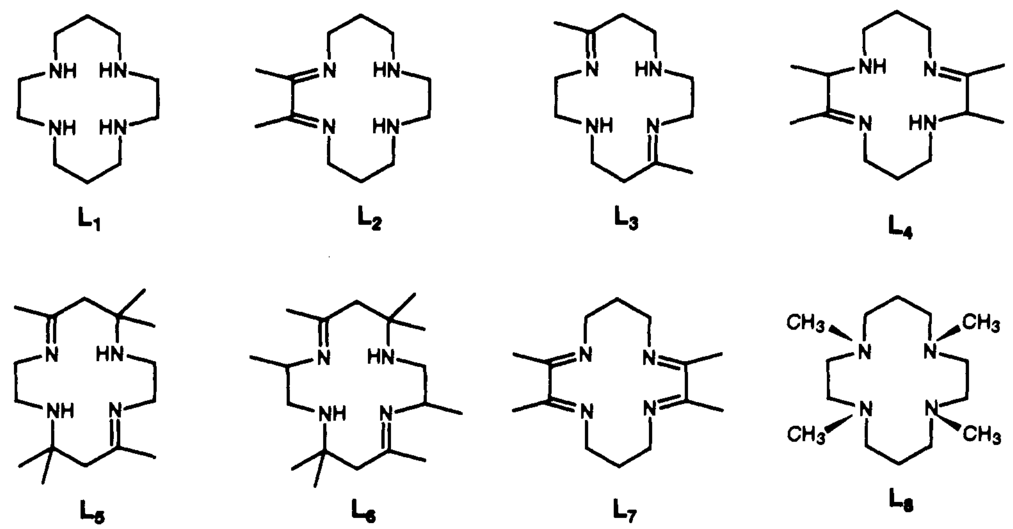

Figure 11. Structures of various 14-membered macrocycles (L_1–L_8).

parable activity for the reduction of CO_2 (runs 22–24), and H_2 evolution increased to some extent. With respect to more extensively C-methylated macrocycles (L_5, L_6), however, the activity in electron mediation of CO_2 reduction decreased by an appreciable extent, but H_2 evolution did not. In addition, there is no enhancement in the production of CO and HCO_2^- when TEA is replaced by TEOA. Furthermore, the photoreactions with $Co^{II}L_5$ or $Co^{II}L_6$ complexes gave poor results as well (runs 29 and 30). Steric hindrance of two pairs of geminate *C*-methyl groups should operate to reduce the accessibility of CO_2 molecules and of ligand exchange of TEA or TEOA with axial Cl atoms.

Further, H_2 evolution dominated when TEA was used as an electron donor with the N–H bond-free 14-membered tetraazamacrocycle, L_7. However, the use of TEOA instead of TEA increased the CO formation to an appreciable extent. These results are rationalized as being due to the poor CO_2-binding ability caused by the absence of N–H groups in the macrocycle and due to the poor reducing power of the intermediary $Co^{I}L_7$ species, as evident from the most positive redox potential, −0.34 V vs SCE in AN.[23] Interestingly, CO_2 photoreduction to CO is enhanced in the presence of TEOA through its coordination with $Co^{III}L_7$. This fact implies that the presence of N–H groups in 14-membered tetraazamacrocycles is not always a requisite for effective CO_2 binding.

With regard to the N-methylated cyclam, L_8, the $Co^{III}L_8$ complex could not be obtained, but the prepared $Co^{II}L_8$ complex did not mediate the photoreduction of CO_2. Only a small quantity of H_2 was detected, and neither CO nor HCO_2^- was produced even in the presence of TEOA. This inactivity may be explained as being due to steric hindrance from the four *N*-methyl groups in CO_2 binding. However, the $Co^{III}L_8$ complex is reported to be very unstable due to the difficulty in attaining the six-coordinate structure of Co^{III} and the very high $Co^{III/II}$ potential ($E_{1/2} > 1.2$ V).[30] $CoCl_2$, which is reluctant to be oxidized to $CoCl_3$, was also inactive for electron mediation (Table I, run 10). Taking these facts into account, the inadequate electron mediation of $Co^{II}L_8$ may be ascribed to the difficulty in reversible formation of the Co(III) species. In other words, the effective electron mediation of cobalt complexes in CO_2 reduction should depend on efficient formation of Co(III) species.

Laser Flash Photolysis. Laser flash photolysis was undertaken to provide evidence for electron transferr from $OPP\text{-}3^{\bullet -}$ to the TEA-coordinated $Co^{III}L_1$, $[Co^{III}L_1(TEA)_2]^{3+}$. As reported previously,[31] the singlet state of OPP-3 (eq 1) is reductively quenched

$$OPP\text{-}3 \xrightarrow{h\nu} {}^1OPP\text{-}3^* \qquad (1)$$

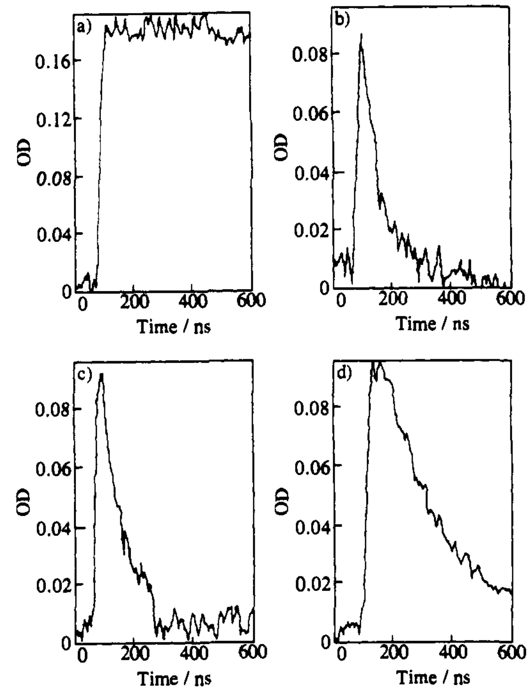

Figure 12. Transient decay curves of $OPP\text{-}3^{\bullet -}$, monitored at 480 nm in TEA/MeOH/AN: (a) without additive; (b) with $Co^{III}L_1$ (1.7×10^{-3} M); (c) with $Co^{III}L_1$ (1.7×10^{-3} M) and CO_2; (d) with $Co^{III}L_1$ (2.5×10^{-4} M) and CO_2.

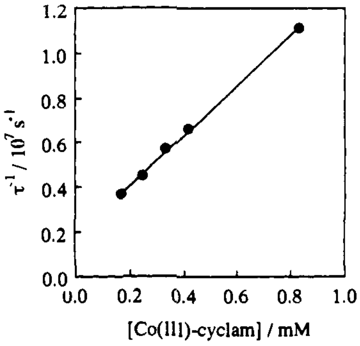

Figure 13. Kinetic behavior of the OPP-3 radical anion, as shown by a plot of the pseudo-first-order rate constant vs $Co^{III}L_1$ concentration.

by TEA to produce the radical anion of OPP-3, $OPP\text{-}3^{\bullet -}$, and the radical cation of TEA, $TEA^{\bullet +}$. The stable formation of $OPP\text{-}3^{\bullet -}$ at 480 nm was observable, as shown in Figure 12a; its lifetime was determined to be 8.3 μs, indicating very stable charge sepa-

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[30] Lee, S.; Bakas, A.; Espenson, J. H. *Inorg. Chem.* **1990**, *29*, 2480.

[31] Matsuoka, S.; Fujii, H.; Yamada, T.; Pac, C.; Ishida, A.; Takamuku, S.; Kusaba, M.; Nakashima, N.; Yanagida, S.; Hashimoto, K.; Sakata, T. *J. Phys. Chem.* **1991**, *95*, 5802.

Table III. Effects of Various Co(III) Complexes on Photochemical Generation of CO, HCO_2^-, and H_2 from OPP-3 and CO_2 in MeOH/AN/TEA or TEOA[a]

			photoproduct formn/(μmol/h)			ratio	
run	complex	$E_{1/2}$[b]	CO[c]	HCO_2^-	H_2	$CO/(HCO_2^- + H_2)$	HCO_2^-/H_2
19	$[Co^{III}L_1Cl_2]Cl$	−1.9	23 (48)	11	3.7	1.6	3.0
20	$[Co^{III}L_1Cl_2]ClO_4$		20 (45)	10	3.5	1.5	2.9
21	$[Co^{III}L_1Br_2]Br$		21 (51)	10	3.6	1.5	2.8
22	$[Co^{III}L_2Br_2]ClO_4$	−0.89	28 (53)	18	5.6	1.2	3.2
23	$[Co^{III}L_3Cl_2]ClO_4$	−1.51	27 (46)	18	7.3	1.1	2.5
24	$[Co^{III}L_4Br_2]ClO_4$	−1.41	25 (42)	13	9.2	1.1	1.4
25	$[Co^{III}L_5Cl_2]ClO_4$	−1.34	10 (7.0)	1.5	7.6	1.1	0.20
26	$[Co^{III}L_5(CN)_2]ClO_4$		9.1 (7.0)	3.5	6.1	0.95	0.57
27	$[Co^{III}L_6Cl_2]ClO_4$	−1.28	5.1 (3.8)	0	6.5	0.79	0
28	$[Co^{III}L_7Br_2]Br$	−0.34	14 (30)	2.2	30	0.43	0.07
29	$[Co^{II}L_5(H_2O)](ClO_4)_2$		9.8 (4.0)	1.4	7.2	1.1	0.19
30	$[Co^{II}L_6(H_2O)](ClO_4)_2$		4.0 (6.6)	0	4.4	0.91	0
31	$[Co^{II}L_8Cl]ClO_4$		0 (0)	0	4.4	0	0

[a] Homogeneous solutions (3 mL) containing OPP-3 (2 mM) and a cobalt complex (1.7 mM) were irradiated at λ > 290 nm for 1 h. [b] $Co^{II/I}$/V vs SCE. [c] In parentheses is the amount of CO produced when TEOA was used instead of TEA.

ration between OPP-3 and TEA as reported previously. In the presence of $Co^{III}L_1$ (1.7×10^{-3} M), the lifetime decreased to 67 ns in either the presence or the absence of CO_2 (Figure 12b,c). When the concentration of $Co^{III}L_1$ was decreased by a factor of 7 (2.5×10^{-4} M), the lifetime of $OPP\text{-}3^{\bullet-}$ increased to 220 ns (Figure 10d). These decay curves were confirmed to follow pseudo-first-order kinetics. A linear plot of the decay rate vs concentration of $Co^{III}L_1$ gave a second-order rate constant $k_s = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$, as shown in Figure 13. On the other hand, the radical cations derived from tertiary amines such as $TEA^{\bullet+}$ and $TEOA^{\bullet+}$ are reported to undergo rearrangement to yield reducing radicals which can also reduce Co(III) species.[32] From these observations, we confirmed that, after the effective formation of $OPP\text{-}3^{\bullet-}$ and $TEA^{\bullet+}$ in methanolic AN (eq 2), the reductive electron transfer should occur subsequently to $[Co^{III}L_1(TEA)_2]^{3+}$, producing $[Co^IL_1]^+$ possibly through $[Co^{II}L_1(TEA)]^{2+}$ (eq 3).

$$^1OPP\text{-}3^* + TEA \rightarrow OPP\text{-}3^{\bullet-} + TEA^{\bullet+} \qquad (2)$$

$$[Co^{III}L_1(TEA)_2]^{3+} \xrightarrow{OPP\text{-}3^{\bullet-}/TEA^{\bullet+}} [Co^{II}L_1(TEA)]^{2+} \xrightarrow{OPP\text{-}3^{\bullet-}} [Co^IL_1]^+ \qquad (3)$$

Mechanism of the Mediation of Co^{III}cyclam ($Co^{III}L_1$) in the OPP-3-Catalyzed Photoreduction of CO_2. With regard to reactions of CO_2 with cobalt complexes, the insertion of CO_2 into Co^IH^- to produce the Co(III)–formate complex[13,33,34] and the direct reactions of CO_2 with Co(I) coordinated with 14-membered tetraazamacrocycles[21–23,35] have been extensively reported. Recently, a theoretical study has been reported on a d^8 Co(I)–CO_2 complex as a model of the well-known η^1-C-coordinated CO_2 complex based on ab initio molecular calculations.[36] On the basis of reported interpretations and the following facts, a mechanism for the $Co^{III}L_1$-catalyzed photoreduction of CO_2 with TEA is depicted as shown in Figure 14. (1) Cobalt macrocycles symbolized as $Co^{III}L_1$ undergo ligand exchange with tertiary amines used as sacrificial electron donors, giving tertiary-amine-coordinated $Co^{III}L_1$ as exemplified by $[Co^{III}L_1(TEA)_2]^{3+}$; (2) the long-lived radical anion $OPP\text{-}3^{\bullet-}$ has such a powerful reduction potential, i.e., OPP-3/$OPP\text{-}3^{\bullet-}$ (−2.45 V vs SCE in dimethylamine),[37] that $Co^{III}L_1$ species can be reduced not only to the Co(II) species ($Co^{III}L_1/Co^{II}L_1$, −0.31 V vs SCE in AN) but also to a Co(I) species ($Co^{II}L_1/Co^IL_1$, −1.9 V in AN (E_{pc}); (3) the initial step is reduction of $[Co^{III}L_1(TEA)_2]^{3+}$ through the electron transfer from $OPP\text{-}3^{\bullet-}$, resulting in the sequential formation of $[Co^{II}L_1(TEA)]^{2+}$ and $[Co^IL_1]^+$; (4) $[Co^IL_1]^+$ can react preferentially with CO_2 to give the intermediary $[Co^IL_1(CO_2)]^+$ or react with a proton to give a d^6 hydride $[Co^{III}L_1(H^-)(TEA)]^{2+}$;[21–23] (5) extensive charge donation from Co(I) to CO_2 in $[Co^IL_1(CO_2)]^+$ may result in electron transfer leading to the formation of $[Co^{II}L(CO_2^-)]^+$; however, such a species has never been characterized; (6) the six-coordinate structure of $[Co^{III}L_1(CO_2^{2-})(TEA)]^+$ may be formed with retention of the stable low-spin d^6 configuration; (7) protonation of $[Co^{III}L_1(CO_2^{2-})(TEA)]^+$ and reduction with an electron from $OPP\text{-}3^{\bullet-}$ and/or the Co(I) species may produce CO, OH^-, and the five-coordinate complex $[Co^{II}L_1(TEA)]^{2+}$, which was successfully confirmed by ESR in the presence of CO_2; (8) N–H protons of the tetraazamacrocycle and β-hydroxylated tertiary amines may serve as ligands to stabilize the adduct of CO_2 with the Co(I) species through bifunctional interactions, i.e., charge-transfer and hydrogen-bonding interactions.[38]

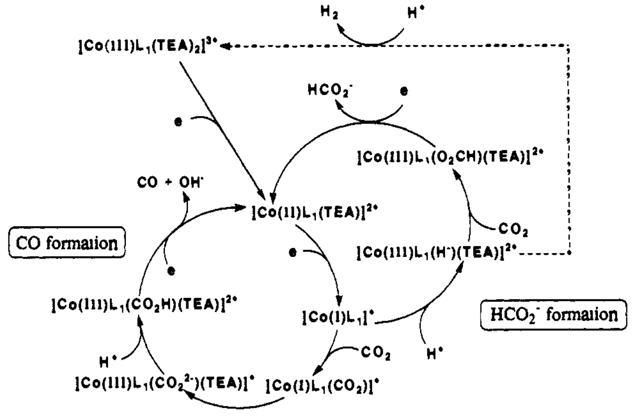

Figure 14. Postulated mechanistic cycle for the OPP-3-catalyzed photoreduction of CO_2 to CO and HCO_2^- mediated by the cobalt–cyclam (L_1) complex coordinated with tertiary amines. As tertiary amines, TEA is exemplified.

Depending on the complex and the conditions, the cobalt center in the CO_2 complexes may be either five-coordinate, like the CO adduct, or six-coordinate. The CO_2 adduct of Co^IL_5 (L_5 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) is thermochromic, evidently existing in a five-coordinate form (purple) at higher temperatures and in a six-coordinate form

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[32] (a) DeLaive, P. J.; Whitten, D. G.; Gianoti, C. *Adv. Chem. Ser.* **1979**, *173*, 234. (b) Chan, S.-F.; Chou, M.; Creutz, C.; Matatsubara, T.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 369.

[33] Misono, A.; Ushida, Y.; Hidai, M.; Kuse, T. *Chem. Commun.* **1968**, 981.

[34] Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 3896.

[35] Gangi, D. A.; Durand, R. R., Jr. *J. Chem. Soc., Chem. Commun.* **1986**, 697.

[36] Sakaki, S.; Dedieu, A. *Inorg. Chem.* **1987**, *26*, 3278.

[37] Meerholz, K.; Heinze, J. *J. Am. Chem. Soc.* **1989**, *111*, 2325.

[38] (a) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405. (b) Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1979**, *18*, 3469. (c) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082. (d) Bianchini, C.; Meli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698.

(yellow) at low temperatures in AN. The ^{1}H NMR and FT-IR spectra of the complex indicate the existence of four diamagnetic CO_2 adducts depending upon whether the solvent is coordinated or not and on whether there is hydrogen bonding between the bound CO_2 and the N–H of the ligand.[39] It is also known that yellow diamagnetic complexes of $[Co^{III}(en)_2(CO_2^{2-})(OH)]^+$ in solution and $[Co^{III}(en)_2(CO_2^{2-})]^+$ in the solid state can be prepared by photolysis[40] of $[Co^{III}(en)_2(ox)]^+$, and the CO_2 adduct (which is stable at pH > 10) decomposes[40b] to form CO and $[Co^{III}(en)_2Cl_2]^+$ in strong acid (4–12 N HCl) and to form CO_2 and Co_{aq}^{2+} at pH 1–6. Although our photocatalytic condition is not the same, it may be reasonable to assume the existence of a $[Co^{III}L(CO_2^{2-})(TEA)]^+$ species, which undergoes reduction to give CO and the recyclable $[Co^{II}L(TEA)]^{2+}$ complex.

As for the formation of HCO_2^-, the mechanism through formation of the Co(III)–formate complex seems to be improbable as a precursor to HCO_2^-. In general, insertion of CO_2 into metal–hydrogen bonds is well-known.[41] Two possible insertion reactions can occur, depending on the polarity of the metal–hydrogen bond: insertion yielding a metal formate (normal type) and reverse insertion producing a metallo carboxylic acid species (abnormal type). Therefore, the formation of HCO_2^- should proceed through $Co^{III}(OOCH)$ formed from the normal insertion of CO_2 into $Co^{III}L(H^-)(TEA)]^{2+}$.

This interpretation is also supported by the following facts: (1) when MeOH was replaced by H_2O, CO evolution decreased, but HCO_2^- formation increased (Table I, run 8); (2) effective formation of H_2 was observed only in the absence of CO_2 in methanolic or aqueous AN systems (Table I, runs 7 and 9) as reported for the $Ru(bpy)_3^{2+}$–Co(II) macrocycle system;[42] (3) the use of unsaturated or methylated cyclam derivatives as ligands was shown to affect selectivities shown by the ratios of $CO/(HCO_2^- + H_2)$ and HCO_2^-/H_2 (Table III). Co(III) complexes with unsaturated cyclam enhanced H_2 evolution because of the lack of the bifunctional binding of CO_2 due to the absence of N–H groups (run 28). Introduction of geminate *C*-methyl groups at the periphery of the macrocycle drastically decreases the ratios of $CO/(HCO_2^- + H_2)$ and HCO_2^-/H_2 (runs 25 and 27). This structural effect can be explained as being due to steric hindrance in the attack of CO_2 molecules.

Cobalt complexes with conjugated diene ligands show several reduction potentials in AN (scan rate = 100 mV s^{-1}, graphite electrode): $[CoL_7Br_2]Br$, −0.075, −0.383, −1.235, and −1.643 V; $[CoL_2Br_2]ClO_4$, −0.060, −0.888, and −1.72 (irreversible, E_{pc}) V vs SCE. When CO_2 is added to the solution, the potentials at −1.643 V for the $[CoL_7Br_2]Br$ complex and at −1.72 V for the $[CoL_2Br_2]ClO_4$ complex were found to shift toward the positive direction because of the formation of stable CO_2 adducts. Although the reduction potentials at −0.383 and −0.888 V have been assigned to the $Co^{II/I}$ couple, the reduced species at these potentials may not be involved in CO_2 binding and reduction. Since the OPP-3 radical anion has very strong reducing power (−2.45 V vs SCE), the cobalt complexes which involve CO_2 activation may be further reduced Co(I) radical species at −1.643 V for $[CoL_7Br_2]Br$ and −1.72 V for $[CoL_2Br_2]ClO_4$.

The failure with $[Ni^{II}L_1]^{2+}$, $[Co^{II}L_8Cl]^+$, and $CoCl_2$ in the catalytic electron mediation in the OPP-3-catalyzed CO_2 photoreduction may result from the very unstable trivalent oxidation states of the metal complexes under our conditions. Although trivalent nickel complexes with tetraazamacrocyclic ligands have been reported[43] and the structure of $[Ni^{III}L_1Cl_2]ClO_4$ has been determined, these complexes are stable only in acidic media. The $Co^{III}L_8$ complex has an oxidation potential at >1.2 V[30] and cannot form six-coordinate species because of steric hindrance by *N*-alkyl groups. The ligation by tertiary amines inhibits oxidation of the free Co(II) ion to the Co(III) ion.[12]

Conclusion

We have now shown that the combination of the OPP-3-catalyzed photosystem with $Co^{III}L$ (L = cyclam or related macrocycles) as an electron mediator in solution induces highly efficient and selective electron transfer for the reduction of CO_2. Smooth electron migration from OPP-3$^{\bullet-}$ to $Co^{III}L$ and/or $Co^{II}L$ complexes plays a decisive role in stabilization of the OPP-3 photocatalyst, and the formation of $Co^IL(CO_2)$ complexes through CO_2 binding with intermediary Co^IL complexes is beneficial for the selective reduction of CO_2 to CO. For construction of artificial photosynthesis, the present findings establish that photoinduced charge separation should be stabilized, and removal of electrons and holes should be effected by introducing suitable electron mediators to CO_2. Design for photocatalysts or photosensitizers and electron mediators producing powerful CO_2-binding and -reducing intermediates should be a requisite for selective photoreduction of CO_2. Molecular design based on this concept would create promising molecular systems for visible-light-driven artificial photosynthesis.

Experimental Section

Materials. *p*-Terphenyl (OPP-3) was obtained from Nacalai Tesque and purified by recrystallization from methanol. $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ were purchased from Nacalai Tesque. TEA, TPA, TBA, TEOA, TIPOA, DEAEO, DEAIPO, DMF, AN, and THF were purchased from Wako Pure Chemical Industries and distilled before use.

Preparation of Metal Complexes. *trans*-Dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) chloride ($[Co^{III}L_1Cl_2]Cl$ or Co^{III}cyclam) was prepared according to the literature.[44] $CoCl_2 \cdot 6H_2O$ (2.4 g) dissolved in methanol (30 mL) was added to a solution of the cyclic amine (2.0 g) in methanol (20 mL), and air was bubbled through the brown solution for 1 h. Concentrated HCl (3 mL) was added, and the color changed to deep green. Air was bubbled through the solution for a further 1 h, and then the solution was filtered and evaporated to dryness. The green residue was recrystallized from the minimum amount of water at 80 °C, and the green needlelike crystals were filtered off and washed with acetone and ether (2.8 g).

trans-Dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) perchlorate ($[Co^{III}L_1Cl_2]ClO_4$) was prepared by adding excess sodium perchlorate to a saturated solution of the chloride and was recrystallized from the minimum amount of hot water.

trans-Dibromo(1,4,8,11-tetraazacyclotetradecane)cobalt(III) bromide ($[Co^{III}L_1Br_2]Br$) was prepared in an analogous way using a $CoBr_2 \cdot 6H_2O$ and HBr solution.

$[Co^{III}L_2Br_2]ClO_4$ (L_2 = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene), $[Co^{III}L_3Cl_2]ClO_4$ (L_3 = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), $[Co^{III}L_4Br_2]ClO_4$ (L_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene), $[Co^{III}L_5Cl_2]ClO_4$, $[Co^{III}L_5(CN)_2]ClO_4$ (L_5 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), $[Co^{III}L_6Cl_2]ClO_4$ (L_6 = 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), $[Co^{III}L_7Br_2]Br$ (L_7 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, $[Co^{II}L_5(H_2O)](ClO_4)_2$, $[Co^{II}L_6(H_2O)](ClO_4)_2$, and $[Co^{II}L_8Cl]ClO_4$ (L_8 = 1,4,8,11-tetramethylcyclam) were prepared as described in the previous paper.[23]

Dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(II) ($Ni^{II}L_1$ or $[Ni^{II}L_1]Cl_2$) was prepared according to the literature.[45] $NiCl_2 \cdot 6H_2O$ (0.29 g) dissolved in warm ethanol (20 mL) was added to a solution of the ligand (0.25 g) in ethanol (10 mL). The resulting light brown solution was warmed on a water bath for a few minutes before ether was added. The resultant mauve precipitate was filtered off and washed with ether. It may be recrystallized by adding ether to the saturated solution in methanol.

Analysis. The CO and H_2 evolved were analyzed by GLC using an activated carbon column (3 m × 3 mm) on a Shimadzu Model GC-12A at 100 °C. The HCO_2^- produced was analyzed by HPLC using a Tosoh anion-exclusion column with aqueous phosphate at eluent (2 × 10^{-3} M), and detection was performed with UV (λ = 210 nm) and conductivity detectors. Analysis of OPP-3 was carried out by GLC using a Shimadzu

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[39] Fujita, E. Work in progress.

[40] (a) Vaudo, A. F.; Kantrowitz, E. R.; Hoffman, M. Z.; Papaconstantinou, E.; Endicott, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 6655. (b) Katz, N. E.; Szalda, D. J.; Chou, M. H.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 6591. (c) Szalda, D. J.; Chou, M. H.; Fujita, E.; Creutz, C. *Inorg. Chem.*, in press.

[41] Vol'pin, M. E.; Kolomnikov, I. S. *Pure Appl. Chem.* **1975**, *33*, 567.

[42] Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.

[43] (a) Gore, E. S.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 1. (b) Ito, T.; Sugimoto, M.; Toriumi, K.; Ito, H. *Chem. Lett.* **1981**, 1477.

[44] Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

[45] Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1109.

Model GC-12A apparatus equipped with a flame ionization detector and a 25 m × 0.2 mm Shimadzu capillary column of OV-1 (carrier gas N_2; carrier gas pressure 1.3 kg/cm^2; column temperature 240 °C; injector temperature 250 °C).

The ESR spectra were measured at 77 K with an ESR spectrometer, JEOL ME-3X, equipped with 100-kHz magnetic field modulation.

Cyclic voltammograms were obtained on a potentiostat (Nikko Keisoku NPOT-2501) with a potential sweeper (Nikko Keisoku NPS-2A) or a BAS 100 instrument by using a glassy carbon working electrode, a platinum foil counter electrode, and a saturated calomel reference electrode (SCE). The working electrode was polished with alumina powder prior to use, followed by washing with twice-distilled water in an ultrasonic bath. All measurements were carried out at 25 °C.

Other analyses were identical with those reported in the previous paper.[31]

Photoreactions. As reported in the previous paper,[31] distilled TEA (0.5 mL), acetonitrile (AN) (2.0 mL), a methanolic solution of $Co^{III}L_1$ (0.5 mL, 5×10^{-3} M), and 10 mg of OPP-3 were placed in a Pyrex tube (8 mm in diameter). After the mixture was purged with CO_2 gas, the tube was closed off with a gum stopper and then irradiated under magnetic stirring at $\lambda > 290$ nm using a 500-W high-pressure mercury arc lamp. For homogeneous runs, the AN solution of OPP-3 (3×10^{-3} M) was used. The gaseous and liquid products were analyzed by GLC and HPLC.

Laser Flash Photolysis. An AN solution containing OPP-3 and TEA (1 M) was placed in a quartz cell and then degassed; [OPP-3] = 1.0×10^{-5} M. Measurements were conducted by means of an excimer laser under conditions similar to those reported.[31]

ESR Measurements. A mixture of an AN solution of OPP-3 (3 mM, 2 mL), a methanolic solution of $Co^{III}L_1$ (10 mM, 0.5 mL), and TEA (0.5 mL) was prepared, and 1 mL of the solution was pipetted into each of two Pyrex ESR tubes. The solution in one tube was saturated with CO_2, and the tube was sealed. The other tube was sealed under vacuum. Two pairs of the above samples were irradiated with a high-pressure 100-W Hg lamp ($\lambda > 290$ nm). Spectra of frozen sample solutions were recorded at liquid-nitrogen temperature in intervals of 5-s irradiation at room temperature or after 5-min irradiation at room temperature. The ESR spectrum in the presence of TEOA was obtained similarly by substituting TEOA for TEA. In order to maintain a nearly identical sensitivity, the same ratio-frequency power of 8 mW incident on the cavity and the same modulation amplitude of 16 G were used throughout. For the measurement of g values, a Mn–MgO probe was employed.

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Copper(I)/(*t*-BuOOH)-Induced Activation of Dioxygen for the Ketonization of Methylenic Carbons

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Abstract: In acetonitrile/pyridine bis(bipyridine)copper(I) [$Cu^I(bpy)_2^+$] activates HOOH and *t*-BuOOH for the selective ketonization of methylenic carbons. With 5 mM $Cu^I(bpy)_2^+$/100 mM HOOH(Bu) the conversion efficiencies [product per 2HOOH(Bu)] for c-C_6H_{12} are 31% (HOOH) and 59% (*t*-BuOOH, argon atmosphere) and for $PhCH_2CH_3$ are 24% (HOOH) and 64% (t-BuOOH, argon). With 5 mM $Cu^I(bpy)_2$ and 10 mM *t*-BuOOH under argon the conversion efficiency for c-C_6H_{12} is 10% and for $PhCH_2CH_3$ is 140%. However, in the presence of O_2 (1 atm, 7 mM) the conversion efficiency for c-C_6H_{12} increases to 67%, and for $PhCH_2CH_3$ to 440% [all PhC(O)Me (22 mM)], respectively. The latter result represents a $Cu^I(bpy)_2^+$/*t*-BuOOH-induced *autoxygenation* with at least 2.2 O_2/catalyst turnovers. In acetonitrile the bis(bipyridine)cobalt(II) [$Co^{II}(bpy)_2^{2+}$] complex in combination with *t*-BuOOH also activates O_2 for the ketonization of methylenic carbons but is about one-half as efficient as the $Cu^I(bpy)_2^+$/*t*-BuOOH combination.

A recent paper[1] summarizes the reaction efficiencies and product selectivities for a group of ML/HOOH(or *t*-BuOOH)/hydrocarbon–substrate systems (ML = seven iron complexes and one cobalt complex) that ketonize methylenic carbons via the initial formation of a hydroperoxide(or *t*-BuOO)–substrate intermediate.[2,3] The reaction efficiencies [product per two HOOH(or *t*-BuOOH) range from 10–80% and usually are greater with *t*-BuOOH. Because the $Co^{II}(bpy)_2^{2+}$ and $Fe^{II}(bpy)_2^{2+}$ complexes provide unique selectivities and good conversion efficiencies,[1,4] we initiated an evaluation of other bipyridine complexes of transition metals (Cu, Mn, Cr, V, Mo, and Ru).

Although copper(II) salts in pyridine activate hydrogen peroxide for the ketonization of methylenic carbons, the reaction efficiencies for all conditions were less than 12% (product per two HOOH molecules).[5] Here we report (a) that bis(bipyridine)copper(I) [$Cu^I(bpy)_2^+$] in acetonitrile/pyridine [4:1 mol-ratio] activates HOOH and *t*-BuOOH for the selective ketonization of methylenic carbons [closely similar to the $Co^{II}(bpy)_2^{2+}$/HOOH(Bu) system][1,4] and (b) that the 1:1 $Cu^I(bpy)_2^+$/*t*-BuOOH combination activates O_2 for the direct ketonization of methylenic carbons.

Experimental Section

Equipment. The reaction products were separated and identified with a Hewlett-Packard 5880A series gas chromatograph equipped with an HP-1 capillary column (cross-linked methyl silicone gum phase, 12 m × 0.2 mm i.d.) and by gas chromatography–mass spectrometry (Hewlett-Packard 5790A Series gas chromatograph with a mass-selective detector).

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(1) Tung, H.-C.; Kang, C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1992**, *114*, 3445.

(2) Barton, D. H. R.; Doller, D.; Balavoine, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1787.

(3) Barton, D. H. R.; Doller, D.; Ozbalik, N.; Balavoine, G. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 3401.

(4) Tung, H.-C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 8214.

(5) Barton, D. H. R.; Csuhai, E.; Doller, D.; Geletii, Yu. V. *Tetrahedron* **1991**, *47*, 6561.

0002-7863/93/1515-609$04.00/0